Pergamon

Tetrahedron, Vol. 52, No. 29, pp. 9945-9952, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00526-1

The Relationship of Classical and Magnetic Criteria of Aromaticity

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Abstract: In contrast to earlier reports good linear relationships are shown to exist between experimental diamagnetic susceptibility enhancements for some 50 aromatic and heteroaromatic ring systems and the corresponding resonance energies and/or aromaticity indices. Consequently there is no apparent justification for separate 'classical' and 'magnetic' concepts of aromaticity as earlier proposed. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

A wide variety of criteria have been proposed for the assessment of aromaticity ranging from the purely qualitative to the virtually quantitative [1]. Several years ago Katritzky *et al.*[2] selected twelve of the most widely employed aromaticity criteria for a small group of heterocycles. These criteria were classified as being of either energetic, structural or magnetic origin and the data were subjected to principal component analysis. The analysis indicated that aromaticity is a multidimensional phenomenon, and this conclusion has been supported by other similar studies [3,4]. However, in contrast to preceding supposition and theoretical analysis [5] it was concluded [2] that "the classical and magnetic concepts of aromaticity are almost completely orthogonal" and that "there are at least two types of aromaticity".

Contrary to this conclusion I had observed an excellent linear correlation between the dilution shift parameters (A) for furan, tellurophene, selenophene, thiophene and benzene and the aromaticity index I_A [6]. The A parameters are clearly magnetic in origin, while I_A has been commended [2,7] as a measure of classical aromaticity. Subsequent to the initiation of the work reported in this paper Schleyer *et al.* [8]. have reported excellent linear correlations between theoretically obtained magnetic susceptibility exaltations and aromatic stabilisation energies for a series of five-membered C_4H_4X ring systems.

In order to clarify the relationship between 'classical' and 'magnetic' criteria of aromaticity it seemed essential to explore the quantitative relationship between appropriate experimental data for as wide a range of aromatic and heteroaromatic systems as possible.

AROMATICITY CRITERIA USED IN THIS STUDY

Resonance energies are by far the most widely accepted of aromaticity criteria. Unfortunately much confusion has arisen in the literature as a result of the use of a variety of different sets of reference bond energies for the calculation of resonance energies. Consequently, all of the resonance energies listed in Tables

2 and 3 have been calculated from literature heats of formation [9] using a Laidler bond energy scheme and a single set of bond energies [6]. In the case of some of the polycyclic hydrocarbons experimental heats of formation are not available and the requisite values were obtained by a reliable group additivity method [10]. An internal cross check on the resulting resonance energies was provided by calculating the value of the resonance integral β using the theoretically deduced [11] values in terms of β. A satisfactory constancy of values was obtained.

In view of the somewhat restricted range of resonance energies available for heterocycles the aromaticity index, I_A, [6] which has now been extended to tricyclic ring systems, was used as an alternative criterion of classical aromaticity This index is based upon a statistical evaluation of the extent of variation of ring bond order provided by the expression

$$I_A = 100F(1 - V/V_K)$$

where $$V = \frac{100}{N}\sqrt{\frac{(N - N)^2}{n}}$$

N is the arithmetic mean of the n various ring bond orders, N, which are readily obtained [12] from the corresponding experimentally determined bond lengths. V_K is the value of V for the corresponding non-delocalised form of the ring. Appropriate values of V_K and the scaling factor F for various ring systems are listed in Table 1.

TABLE 1. Factors for Calculation of Aromaticity Indices.

Ring Size	V_K	F
5	35	1.235
5,6	35	2.085
6,5,6	35	2.97
6	33.33	1.0
6,6	34.23	1.84
6,6,6 (linear fused)	34.51	2.66
6,6,6 (angular fused)	34.51	2.72

In the light of the original. study [2] diamagnetic susceptibility exaltations and ^{15}N nmr shifts of ring nitrogen atoms were selected as the magnetic criteria. The diamagnetic susceptibility exaltations [13] were calculated from reported [13,14] diamagnetic susceptibilities using the Haberditzl "Semi-Empirical Increment System". This method assigns a susceptibility increment to each type of bond and electron grouping. Summation of these increments yields the predicted magnetic susceptibility. The difference between the predicted and observed susceptibilities is termed the susceptibility exaltation, Λ.

Chemical shifts of both ring atoms and proton substituents have been used as criteria of aromatic properties [1]. In most cases measurements have been recorded by a wide range of laboratories using a variety of solvents. Fortunately ^{15}N nmr chemical shifts have been recorded [15] for a wide range of nitrogen heterocycles under standard conditions in dimethyl sulfoxide. These data have been employed for the present

TABLE 2. Aromaticity Criteria for Carbocyclic Compounds

Compound	R.E. Kcal/mole	β Kcal/mole	Λ $-10^{-6}cm^3mol$
Fulvene	1.9	-	1.9
Benzene	45.8	22.9	14.5
Styrene	52.8	-	12.6
Naphthalene	80.3	21.8	27.4
Azulene	47.1	-	26.5
Biphenylene	44.95	-	13.8
Biphenyl	94.7	21.6	25.1
Acenaphthylene	82.8	-	37.4
Stilbene	103.5	-	26
Anthracene	111.5	21.0	42.4
Phenanthrene	117.1	21.5	40
Fluoranthrene	126.3	-	40.4
Pyrene	141.4	21.7	57.4
p-Terphenyl	143.5	21.2	36.7
Tetracene	147.6	21.3	56.7
Acenaphthanthracene	151.2	-	63
Triphenylene	151.7	20.9	45.3
Chrysene	152.8	21.3	55.7
Perylene	172.3	20.9	45.8
Benzo[a]pyrene	176.8	-	73
Pentacene	183.2	21.4	70.7
Dibenz[a,h]anthracene	187.6	21.3	58.3
Dibenz[c,g]phenanthrene	187.6	21.0	81
Anthanthrene	200.4	-	73.5
Dibenzpyrene	213.4	-	69.2
Coronene	226.0	21.4	102.9
Pyranthrene	266.7	-	85.4
Dibenzocoronene	288.4	-	115.9
Ovalene	294.0	-	170.6
Hexabenzocoronene	305.9	-	106.3
Violanthrene	323.6	-	118

TABLE 3. Aromaticity Criteria for Aromatic and Heteroaromatic Compounds

Compound	R.E.[$]	I_A	Λ [*]	δ (-NMe)$^+$	δ (-N=)$^+$
Furan	27.2	53	8.9	-	-
Thiophene	43.0	81.5	13.0	-	-
Pyrrole	34.8	85	10.2	-230.1	-
Isoxazole	34.	52	13.1	-	2.7
Oxazole	26.2	47	10.4	-	-127
Thiazole	42.0	79	11.6	-	-57.4
Pyrazole	40.4	90	11.4	-180	-80
Imidazole	40.0	79	12.3	-217	-118.1
1,3,4-Thiadiazole	-	80	10.8	-	-10
1H-1,2,3-Triazole	-	90	-	-143.3	-16,-28
2H-1,2,3-Triazole	-	109	-	-135	-54
1H-1,2,4-Triazole	48.3	100	-	-171	-82,-127
4H-1,2,4-Triazole	-	81.5	-	-218	-60
1H-Tetrazole	49.4	100	-	-151	13,-11,-50
2H-Tetrazole	48.1	107	-	-102	-1,-47,-73
Benzene	45.8	100	14.5	-	-
Pyridine	43.3	86	13.5	-	-63.5
Pyridazine	32.7	79	13.1	-	20.2
Pyrimidine	40.6	84	12.7	-	-84.5
Pyrazine	40.9	89	-	-	-46
1,3,5-Triazine	44.9	100	19.5	-	-98.5
Benzofuran	55.4	94	22.2	-	-
Indole	73.8	146	24.2	-254	-
Benzoxazole	-	79	22.2	-	-131.5
Benzothiazole	-	119	26.1	-	-64.7
1H-Indazole	75.7	144	18.1	-204	-57.6
2H-Indazole	73.3	-	-	-162	-92.3
Benzimidazole	78.9	148	16.6	-236	-136
1H-Benzotriazole	77.6	148.5	-	-161.5	-1,-41
2H-Benzotriazole	76.1	159	-	-116.8	-62.6
Naphthalene	80.3	142	27.4	-	-
Quinoline	81.0	134	26.85	-	-67.2
Isoquinoline	81.0	133	24.75	-	-69.3

Table 3 (cont.)

Cinnoline	70.3	130	-	-	-41,-44
Quinazoline	76.5	143	-	-	-86.5,-98
Quinoxaline	75.3	132	-	-	-50
Phthalazine	70.3	136	-	-	-10
Carbazole	111.7	207	33.2	-273	-
Anthracene	111.5	206	42.4	-	-
Acridine	108.3	198	40.75	-	-74.4
Phenazine	110.3	188	-	-	-53.9
Phenanthrene	117.1	210	40.0	-	-
Phenanthridine	119.6	206	-	-	-70.8
Benzo[f]quinoline	121.9	-	-	-	-67.5
Benzo[h]quinoline	122.7	185	-	-	-76.8
Benzo[c]cinnoline	106.3	194	-	-	-60.9

$ Kcals mole^{-1} ; * -10^{-6}cm^{3}mole^{-1} ; + ppm. relative to nitromethane

study. The chemical shifts used for 'pyrrolic' nitrogens are those observed for the *N*-methyl heterocycles thereby avoiding any ambiguity due to tautomerism or hydrogen bonding. In the original paper [2] the average chemical shift for all of the nitrogens in the ring was employed. For the purposes of the present study it appeared more appropriate to treat them separately.

RESULTS AND DISCUSSION

The relevant data are listed in Tables 2 and 3. Scatter plots for the diamagnetic susceptibility enhancements, Λ, versus resonance energies, R.E. , and the unified aromaticity index, I_A , are shown in Figures 1 and 2. Least squares treatments lead to the relationships $\Lambda = 0.43$ R.E. ($r = 0.95$) for 58 data points, and $\Lambda = 0.17\ I_A$ ($r = 0.89$) for 27 data points. As anticipated there is also a good linear relationship between I_A and R.E., cf. Figure 3;- I_A =1.83 R.E. ($r = 0.88$) over the presently extended range of 37 values. An important point to emphasise is the small range of Λ for monocyclic compounds - a range of six units would encompass all of the azoles and represents the difference between observed and estimated diamagnetic susceptibilities of magnitudes *ca.* 30 -40 units. While it is difficult to assign the 'accuracy' of the estimated magnetic susceptibilities it would seem unreasonable to expect the derived Λ values to be better than *ca.* 1-2 units so that they are rather imprecise criteria of relative aromaticities amongst closely similar groups of compounds. In contrast the plots of R.E. , I_A or Λ against ^{15}N nmr shifts for either azine, =N-, or imine, -NMe- , nitrogens as shown in Figures 4 to 7 were completely random and led to 'best straight lines' with r *ca.* 0. Closer inspection of the ^{15}N nmr data shows that the magnitude of the nitrogen shift is comparitively insensitive to the extent of the aromatic system as instanced by the sequence pyridine -63.5, quinoline -67.2, acridine -74.4 and pyrrole -230.1, indole -253.6, carbazole -272.7. However, introduction of other heteroatoms into the same ring results in large ^{15}N nmr shifts even though changes in R.E. or I_A are small. Thus, although ^{15}N chemical shifts are

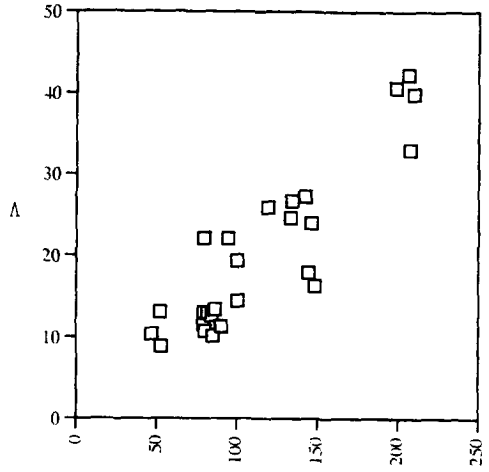


FIGURE 1

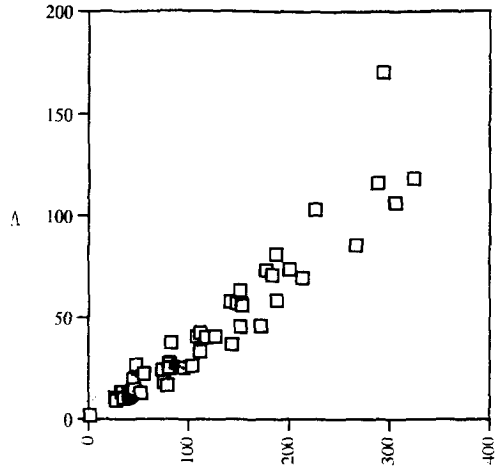
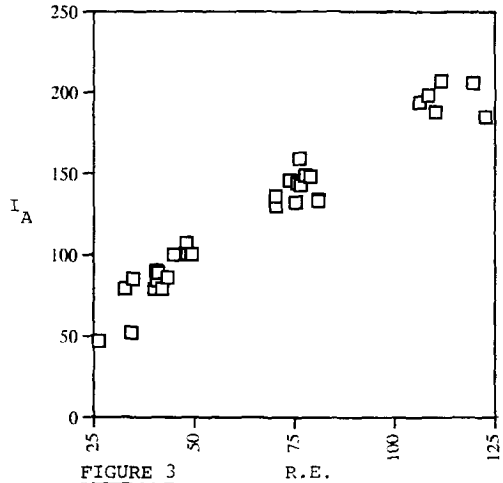


FIGURE 2



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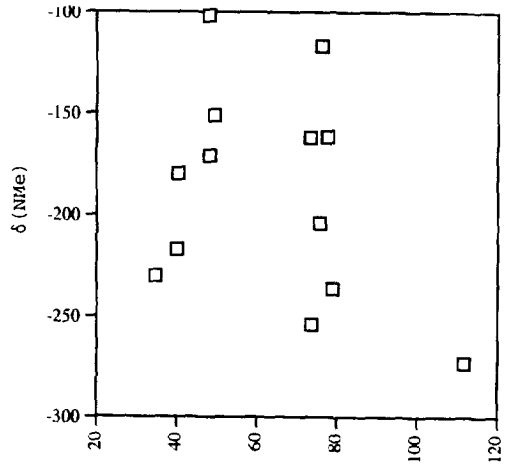

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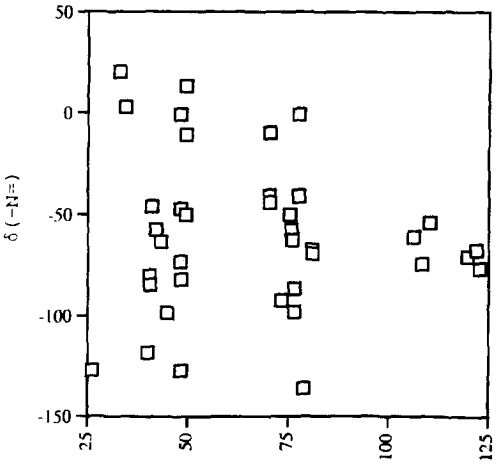

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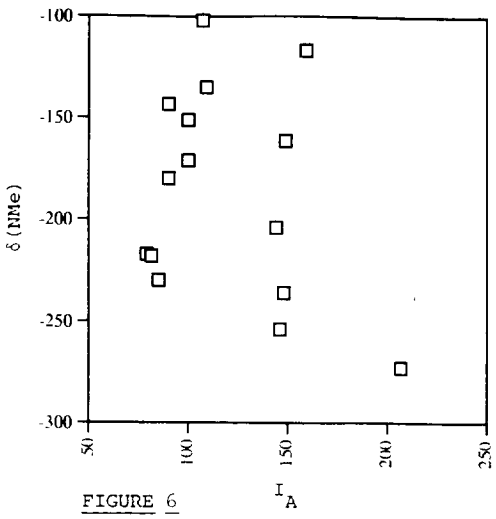

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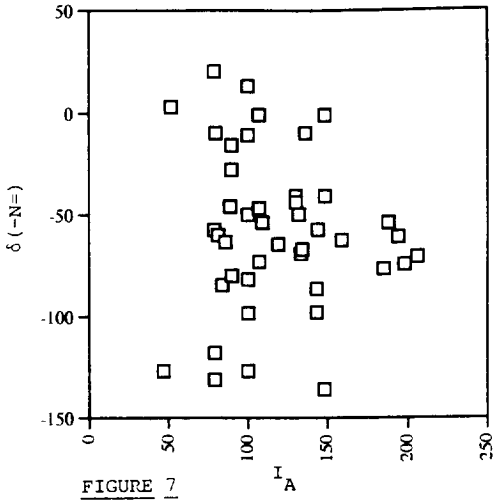

FIGURE 7

affected by ring currents, the magnitude is heavily outweighed by other structural features. In our opinion it is this fact and the foregoing limitations of Λ values which misled the earlier investigators.

CONCLUSION

The experimentally derived data presented in this paper concur with a recent theoretical analysis[8] in demonstrating that 'classical' and 'magnetic' concepts of aromaticity are not 'orthogonal' as proposed[2] earlier.

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(*Received in UK* 13 *May* 1996; *revised* 28 *May* 1996; *accepted* 30 *May* 1996)